SUPERCRITICAL SEPARATION IN AQUEOUS COAL LIQUIFACTION WITH IMPREGNATED CATALYST

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ABSTRACT

Illinois No. 6 coal is liquified using supercritical water as solvent and stannous chloride or molybdenum trisulfide catalyst impregnated in the coal at 640-673 K, hydrogen charge pressures of 2.6-5.4 MPa, and system pressures of 22.3-34.6 MPa. Hydrogen consumption is 0.3-2 g/g coal. Yields of gases and liquids to 54 wt % maf are attained. Supercritical water distillation quantitatively separates the oil and asphaltenes from the coal char, producing a friable residue from sized (3.2 mm) coal in batch tests.

INTRODUCTION

Major factors impeding the commercialization of direct liquifaction of coal are the cost of the hydrogen needed to produce a good product slate, solid-liquid separation difficulties, and the physical isolation of the coal surfaces and supported catalysts. The goal of this work is to advance a coal liquifaction process that resolves or reduces the impact of these factors.

The use of a catalyst soluble in a coal liquid solvent allows for direct impregnation of coal interstices with hydrogenation catalyst. Catalysts that are soluble in organic liquid and that are effective in hydrogenation are rare. In contrast, many hydrogenation catalyst species are soluble in water. Consequently, water is selected as the solvent for the coal liquifaction process. Upon heating a catalyst-water solution in contact with coal into the supercritical region, catalyst is precipitated onto the coal surfaces and into its interstices. Thus the need to employ a hydrogen carrier species is negated.

Some hydrogen for the hydroliquifaction and gasification reactions can be generated in situ by carbon-water reaction, though it is realized that temperatures near the 647 K critical temperature of water are lower than the 820^+ K temperatures used for producing reducing gas by the carbon-steam reaction. It is necessary to add extra hydrogen to the reactor to increase its partial pressure in order to increase yield and decrease viscosity of liquid product. The addition of carbon monoxide or synthesis gas in lieu of hydrogen serves the same purpose, with hydrogen being formed in the reactor by the water gas shift reaction at 670-770 K. The use of water as the coal liquifaction solvent can reduce the cost of producing hydrogen for the coal liquifaction plant.

As the coal liquifaction reaction proceeds, the liquid produced is extracted into the supercritical water and shouldn't remain or be precipitated as a separate phase. At the end of the reaction, the water is simple distilled in the supercritical state from the coal residue, carrying the coal liquid overhead and effecting a solid-liquids separation.

Towards the end of the distillation of the aqueous phase from the coal residue, the water is allowed to pass into the subcritical state where it can back extract or leach catalyst from the char. If sized coal, rather than powdered coal, is employed and suspended in a basket in the reactor, the catalyst precipitates from the water upon evaporation to dryness as a separate solid phase from the suspended coal char product. The catalyst is intermixed with some fines formed during the reaction. These fines can be extracted by water for catalyst recovery.

Either a continuous or a batch process may be developed, though with a batch process the use of powdered coal can result in an unacceptable agglomerated chunk of coal char as the solids product. The use of sized coal in the batch process can result in the production of a friable coal char product.

Desired products from this direct liquifaction process include: (1) fuel gas enriched in sulfur, (2) desulfurized coal liquid, and (3) dry, friable, combustible desulfurized char.

The work reported in this paper differs from previous works in that a combination process of coal liquifaction with hydrogen and impregnated catalyst, extraction into supercritical water, and distillation with supercritical water to separate oil, coal char, and catalyst is used. The combinations of coal nature and size, reductant, catalyst, reactor material, and water density in the reactor are different than in the previous works.

RELATED PREVIOUS WORK

Volatility and Solubility Amplification with Supercritical Fluids

It is well established that supercritical gaseous phases are capable of taking up classes of compounds under supercritical conditions, the amount of material being taken up by the supercritical gas being many times greater than would have been expected from the vapor pressure of these compounds at the temperature of the treatment. Zhuse and Yushkevich (1) reported this phenomenon for the extraction of a crude oil into methane. Studiengesellschaft Kohle m.b.H. (2) obtained patent coverage for a variety of separations based on supercritical gas extraction. Paul and Wise (3) presented an overview of the subject area. Gangoli and Thodos (4) reviewed supercritical gas extraction for recovering liquid fuels and chemical feedstocks from coal. Panzer *et al.* (5) reported on the supercritical gas extraction of the constituents in a tar sand and a peat.

The data of Zhuse and Yuskevich (1) show that increasing pressure increases the solubility of a Russian crude in methane (T_c = 191 K, P_c = 4.64 MPa) at 313 K and that the solubility decreases as the percent stripped increases due to the decreasing vapor pressure of the residue. Solubilities of the crude in the vapor are 30 g/ℓ at 20 MPa, 80 g/ℓ at 50 MPa, and 220 g/ℓ at 80 MPa (790 atm). Up to 90% of the oil could be stripped at 80 MPa.

Zhuse and Yuskevich (6) also show that the nearness to the critical temperature affects the gas phase solubility. With fuel oil residue at 378 K, a vapor phase concentration of 0.7 g/ℓ (upon expansion to standard T and P) is reached at a pressure of 9 MPa with propane (T_c = 370 K, P_c = 4.26 MPa) and propene (T_c = 365 K, P_c = 4.62 MPa), whereas a pressure of 50 MPa is needed with ethylene (T_c = 283 K, P_c = 5.12 MPa).

Studiengesselschaft Kohle m.b.H. (2) reported the effect of temperature on solubility level in supercritical gas. The solubility is highest within 20 K of the critical temperature and decreases as temperature is raised to 100 K above the critical temperature. At temperatures near the critical temperature, a sharp rise in solubility occurs as the pressure is increased to the vicinity of the critical pressure and increases further as the pressure is further increased. Less volatile materials are taken up to a lesser extent than more volatile materials, so the vapor phase has a different solute composition than the residual material. There does not seem to be substantial heating or cooling effects upon loading of the supercritical gas. It is claimed that the chemical nature of the supercritical gas is of minor importance to the phenomenon of volatility amplification. Ethylene, ethane, carbon dioxide, nitrous oxide, propylene, propane, and ammonia were used to volatilize hydrocarbons found in heavy petroleum fractions.

Supercritical hydrocarbons such as 2,2,4-trimethylpentane have been shown by Barton and Hajnik (7) to be capable of quantitatively vaporizing heavy hydrocarbon fractions, such as C_{16}-C_{32} lubricating oil, at 510-580 K. The concentration of oil in the vapor phase changed from 10 to 90 g/ℓ upon crossing the critical pressure (2.57 MPa).

Panzer *et al.* (5) extracted Athabasca tar sand in two steps, the first with compressed *n*-pentane (T_c = 470 K, P_c = 3.37 MPa) and the second with compressed benzene (T_c = 563 K, P_c = 4.92 MPa). At 533-563 K and 2.0-7.7 MPa, *n*-pentane extracted 95% of the maltenes and asphaltenes from the tar sand, whereas at atmospheric pressure only 75% was extracted. Further extraction with benzene at 633 K and 2.0 MPa removed the remaining higher molecular weight asphaltenes. This indicates that the chemical nature of the dense gas is important in some applications.

The large changes in the activities of the constituents of a mixture at and adjacent to the critical temperature and pressure of one of the constituents has been demonstrated by Powell (8). He extracted water from sulfuric acid solutions containing metal salts using n-heptane as the supercritical solvent. An exponential increase in the volatility of water occurred at the critical point of n-heptane, followed by a substantial decrease as the temperature is raised 20 K above the critical temperature of n-heptane.

The solubilities of aromatic hydrocarbons in liquid water have been shown by Barton and Fenske (9) to exceed 8 wt % at temperatures above 590 K which indicates that water should be a good solvent for coal liquids.

Coal Liquifaction

Weller (10) reported on the hydrogenation of Rock Springs, Wyoming, high-volatile C bituminous coal with catalyst impregnated from aqueous solution. The hydrogenations were performed after drying the impregnated coal and without a vehicle solvent. The cold hydrogen pressure was 6.9 MPa, and the reaction time was 1 hour at 723 K. Ammonium molybdate (1 wt % Mo(VI)) and stannous chloride (1 wt % Sn) were shown to be superior catalysts. The following yields were attained: 14-15% gaseous hydrocarbon, 41% oil (hexane soluble), and 20-27% asphaltenes (benzene soluble) based on maf coal.

Stewart and Dyer (11) obtained a patent for thermal cracking of bituminous coal in the presence of supercritical water. Recommended operating parameters include: communition of the coal to 100-200 Tyler mesh, water to coal weight ratio of 1 to 2, hydrogen to coal weight ratio of 0.01 to 0.04, water plus hydrogen pressure from 24.8 to 35.5 MPa, temperature from 670 to 770 K, and reaction time from 1 to 5 minutes. Conversion of carbonaceous material to organic liquid is 20-25%.

Modell et al. (12) reacted bituminous coal (170-200 Tyler mesh) containing 4.95% sulfur slurried in supercritical water at >647 K and 22.8 MPa at a water to coal wt. ratio of 22 for 60 minutes. Conversion to gas was 8% and to liquid was 20% with little formation of char. The gas contained the following constituents in vol. %: 12 H_2, 30 CO, 37 CO_2, 10 CH_4, 1 C_2H_4, 2 C_2H_6, 8 H_2S. Note the in situ generation of hydrogen. About 80% of the sulfur in the coal feed was precipitated in the water as elemental sulfur or released as H_2S. They also reacted glucose in similar fashion using Ni, Pt, and Co-Mo supported catalysts to promote hydrogenation, steam reforming, or cracking.

Ross et al. (13) reported on the application of CO/H_2O chemistry to the conversion of bituminous coal with Na_2MoO_4 and KOH catalysts. Reaction conditions are as follows: Illinois No. 6 coal, -60 mesh, water to coal weight ratio of 3.6, CO (or H_2) charge pressure of 4.9 MPa, KOH charge concentration to 4M, Na_2MoO_4 charge concentration to 0.02M, reaction temperature of 673 K, and reaction time of 20 minutes. The water density at reaction conditions is 0.12 g/cc, which is below the density of 0.317 g/cc for water at its critical point. Substantial hydrogen generation occurred in situ, apparently via the water gas shift reaction. Hydrogen production is promoted by the KOH in the presence of coal and catalyzed by the Hastelloy C reactor walls. Mo was found to be a true catalyst for coal conversion, with a turnover number of ≥ 51. Molybdate was more effective with CO than with H_2 as the charge gas. The yield of benzene soluble material ranged from 38 to 48 wt % of ash-free coal. The benzene-insoluble material ranged from 35 to 47 wt % (presumably the gaseous product ranged from 11 to 15 wt %).

Ross and Nguyen (14) reported that, in coal liquifaction in aqueous suspensions containing trace amounts of metal ions and using carbon monoxide as reductant, the liquifaction yield was found to depend very sharply on the initial pH of the solution. Very high yield of benzene solubles was obtained when the initial pH was larger than 12.6. Addition of potassium formate allowed high liquifaction yield even when the pH was 7.

EXPERIMENTAL PROCEDURES

The apparatus used for performing the coal liquifactions is shown in Figure 1. The reactor has a volume of 3850 cc, is constructed of 316 stainless steel, has a magnetically driven stirrer, contains a basket to hold granular coal, is heated by a thermostatically controlled heating jacket, and has a cooling coil for shutdown. After addition of coal, water, and catalyst, the reactor was assembled and purged with argon. Hydrogen and/or carbon monoxide was then added to the desired initial partial pressure.

The reactor and its contents were heated and maintained at the desired reaction temperature. Additional hydrogen was added in latter runs using a compressor. The reaction products were then distilled from the hot reactor into a 4.55-liter pressure vessel wrapped with a cooling coil. The gaseous and liquid products were separated in this receiver. The gas was removed through a gas meter to a vent. Samples of the gas were collected in 8070 cc evacuated stainless steel vessels. The reactor was then cooled and disassembled to recover the coal residue in the basket and the fines and catalyst residue in the bottom of the reactor.

The gas sample vessels were equipped with heating jackets to provide additional positive pressure for sample recovery during analysis. The hydrogen content was determined with an Orsat analyzer. Gas chromatography with helium carrier gas and thermal conductivity detector was used to analyze the product gas for most of its other constituents. A 5A molecular sieve column at 373 K was used to analyze for argon (purge gas), carbon monoxide, and methane. Injections of pure methane were used for calibration. A hexamethylphosphoramide column at 303 K was used to analyze for carbon dioxide and C_2 to C_5 hydrocarbons. Injections of pure ethane were used for calibration. Relative thermal response values are available for each constituent. Ammonia was analyzed by bubbling a sample of product gas through hydrochloric acid solution to recover the ammonia, releasing the ammonia by increasing the pH to 12^+ and hot stripping the solution with nitrogen gas, trapping the ammonia from the nitrogen stripping gas with standardized hydrochloric acid solution, and back-titrating the acid solution with standardized sodium hydroxide solution to a pH of 5. Hydrogen sulfide was analyzed by the calcium sulfate-iodometric titration method (ASTM D2385-66).

The distilled reaction liquids were decanted into an organic layer and an aqueous layer. The organic liquid and coal residue were analyzed by Soxhlet extraction using paper thimbles with first n-pentane, then benzene, and finally pyridine using a procedure described by Furman (15). These incremental solubility levels determine the oil, asphaltene, and preasphaltene contents, respectively. The aqueous solubles were concentrated by distillation of the aqueous layer. Elemental analyses (CHNS) were performed on the coal chars using a furnace-gas chromatograph analyzer. An atomic absorption spectrophotometer was used to analyze the liquid and solid samples for catalyst content; the samples were prepared by ashing followed by digestion into acid.

Illinois No. 6 bituminous coal for use in this study has been provided by Oak Ridge National Laboratory in two screened sizes, 3.2 mm and powdered. The coal charge samples were stored and transferred in an argon atmosphere and were not dried. The moisture content of the coal is 5.5 wt. % and its ash content is 12.4 (powd.) or 13.7 (3.2 mm) wt. %. The volatile matter content of a sample of Illinois No. 6 coal used at Oak Ridge is reported to be 48.1% on a moisture and ash free basis (16).

OPERATING CONDITIONS

Seven liquifaction runs were made with Illinois No. 6 coal using supercritical water as the solvent and either stannous chloride or molybdenum trisulfide as the hydrogenation catalyst. The operating conditions are given in Table 1.

The coal charge to the 3.8ℓ vessel varied from 78 to 488 g. It was slurried with the water when powdered or placed in the basket when 3.2 mm particles were employed. The catalyst concentration varied from 0.2 to 2.8 wt % in aqueous solution, or 2.5 to 5.5 wt. % of the coal charged. The disposition of the catalyst is not known after the water becomes supercritical. In Runs 2, 3, and 4 it remains slurried with the powdered coal. In Runs 1, 5, 6, and 7 with 3.2 mm coal, only a portion of the catalyst is expected to be precipitated on or within the coal.

Hydrogen was added at H to coal weight ratios of 0.011 to 0.144, with initial cold pressures of 2.6 to 5.4 MPa. Upon heating the system to 640-673 K, the system total pressure is increased to 22.3-34.6 MPa. The hydrogen "partial" pressure is also increased, e.g. from 4.6 to 6.4 MPa in Run 7. The water density at reaction conditions ranged from 0.13 to 0.28 g/cc, as compared to the critical density of water of 0.317 g/cc.

The heatup time for the reactor was 1.2-1.6 hours; the time the reactants were maintained near the critical point of water was 1.6 to 3.9 hours. In Runs 1, 4, 5, and 7 the product gases and liquids were distilled slowly from the reactor while hot. In Run 2, only part of the fluids were removed while hot. In Run 3, the reaction mixture was cooled down before separating the phases. In Run 6, the gases and liquids were instantaneously vented when a blowout disk ruptured.

RESULTS

Gas yields and analyses are listed in Table 2. Liquid and solid product yields and analyses are listed in Table 3. Material balance data are presented in Table 4. Elemental analyses are given in Table 5.

The yield of gas removed from the reactor ranged from 2.4 to 4.7 gmol; this gas consisted of 74-78 mole % hydrogen. The total gas analyses in Table 2 are based on independent analytical procedures and the results are presented without normalization to indicate possible error range. The yield of gas produced (H_2, A, N_2, H_2O free) ranged from 0.1 to 0.7 gmol. On a moisture and ash free basis the gas yield values were 6 to 11 g/100 g maf coal. The C_1 to C_5 hydrocarbon content of the produced gas was 45 to 55 mole %. The yield of hydrocarbon decreased with increasing molecular weight, ranging from 18 to 30 mole % C_1 to 2 to 5 mole % C_4 + C_5.

The carbon dioxide (plus carbon monoxide) content of the gas produced is quite high at 35 to 54 mole % (Table 2). Whether any of this could have been produced by carbon-water reaction, as contrasted to being produced by cracking of the coal, is not known. The amount of carbon dioxide (plus carbon monoxide) product ranged from 2.7 to 4.3 g/100 g undried coal (Table 4). The oxygen content of the carbon oxides produced is less than the oxygen content of the coal of 10-11 wt. % (dry, excluding that in the ash).

The net hydrogen disappearance per unit mass of coal is reported in Table 4, based on gas material balance. The best gas phase material balances reported are for Runs 5 and 7; the hydrogen disappearance was 0.28-1.9 g/100 g undried coal, or 0.35-2.3 g/100 g maf coal, respectively. Hydrogen consumption was higher in Run 7 than in Run 5 because reaction temperature and hydrogen partial pressure were higher. A hydrogen balance for Run 5 using the analyses in Tables 2, 4, and 5 gives 4.57 g H in and 4.23 g H out per 100 g undried coal, which is within 7% of the above value based on hydrogen analyses.

Ross et al. (13) reported hydrogen uptakes of 1.1 to 1.3 g/100 g dried coal in liquifaction of Illinois No. 6 coal in the presence of water, Na_2MoO_4 or KOH catalyst, and CO reductant at 673°K and 4.9 MPa charge pressure with a 20 minute reaction time. They report lower hydrogen uptake with Na_2MoO_4 and H_2 reductant. Hydrogen uptakes in the present work are comparable to their data.

The distribution of product yields between aqueous liquid, organic liquid, and solid residue in Table 3 are adjusted to a common coal weight basis in Table 4. The aqueous products contained soluble material separable by distillation. This represented up to 2% of the coal charge. In Run 4, 1% of the coal charge was collected overhead in an organic layer from a simple redistillation of the aqueous product. Some of the remaining soluble material in the redistillation of the aqueous phase is collected as a solid residue. A water balance for Run 5 gives 430 g H_2O in as water charge and with the coal and 425 g out in gaseous, aqueous, and organic products, per 100 g undried coal, which agree by 1 %. Negligible catalyst (<10 ppm) was entrained overhead with the aqueous product from the supercritical distillations. In Runs 2 and 3 in which the coal char and water product were cooled together, it was assumed that most of the catalyst extracted into the water phase in computing the material balances;

however, Ross et al. (13) found evidence that much of the molybdenum remains in the coal phase with this type of product recovery.

The material listed as organic "liquid" product includes that decanted from the aqueous product, recovered by redistillation of the aqueous product, scraped from the reactor and receiver walls, and recovered by distillation of acetone used to wash the vessels. The composite "liquid" ranges from semisolid at room temperature for runs with low hydrogen uptake to lube oil consistency with increased hydrogen uptake. The yield ranged from 11 to 25 g/100 g undried coal, or 13 to 31 g/100 g maf coal, with the higher value corresponding to the higher hydrogenation severity of Run 7. The organic liquid decanted from the aqueous product in Runs 4 and 5 contained 71-74 wt. % oil, 23-27 wt. % asphalthenes, and 1-3 wt. % preasphalthenes for totals of 98-100 wt. % as determined by incremental solubility in pentane, benzene, and pyridine, respectively. The oil content was increased to 87 wt. % in Run 7, with the remainder of the material being soluble in benzene. In Run 3 where the organic material was not subjected to supercritical distillation but simply decanted from the cooled reactor product, the total solubles in benzene (which includes pentane solubles) is lower at 43 wt. %; this is probably due to the entrainment of solid fines into the organic layer. The capability of supercritical water for removal of oil and asphalthenes by volatilization from coal char is demonstrated by these results.

The coal char products ranged from agglomerated hard piles when using powdered coal feed to friable porous disks when using 3.2 mm coal in the basket. The amount of fines (including catalyst) recovered from the bottom of the reactor when using the 3.2 mm coal in the basket represented 4 to 13 wt. % of the solid product. The coal char from the basket in Run 5, from which the coal tar had been removed by supercritical water distillation, contained 1 wt. % oil, 2 wt. % asphaltenes, and 12 wt. % preasphaltenes. In Run 7 with the water density only 41% of the density at the thermodynamic critical point, the oil, asphaltene, and preasphaltene contents increased to 2, 8, and 23 wt. %, respectively. The agglomerated coal residue from the distillation in Run 4 in which powdered coal was used contained more oil (6 wt. % pentane solubles) than in Run 5. This was retained probably due to difficulty in mass transfer from the large solidified disk of char. The solids products from which the tars were not removed, or incompletely removed, while hot contained 20-21 wt. % material soluble in benzene or acetone (Runs 2 and 3). These data show that supercritical water extraction and distillation provides quantitative removal of oil and asphaltenes from coal char.

The yields of coal char (minus catalyst) ranged from 65-81 g/100 g undried coal with incomplete supercritical distillation removal of tar to less than 61 g/100 g undried coal with complete supercritical distillation removal of tar. The yield of char in Run 7 would have been reduced from 51 to 47 g/100 g had more water closer to supercritical density been available for distillation recovery of tars from it. When the char yield is added to the yield of gas and liquid, and adjusted for the water and hydrogen material balances, the sum of the yields in Table 4 should equal 100. In Run 5, the yield summation is 86 g/100 g undried coal, so 14% or 33 g of product is not accounted for. In Run 7, the yield summation is 92 g/100 g undried coal, so 8% or 17 g of product is not accounted for. Most of the missing material is probably in the gas and liquid yields. Using the moisture and ash analyses in Table 5, the yield of char in Run 5 of 61 g undried char per 100 g undried coal becomes 61 g of maf char per 100 g of maf coal.

Based on minimizing the yields of coal char, stannous chloride and molybdenum trisulfide appear to be equally effective in gasifying and liquifying coal (compare Runs 1 and 5). Increasing the hydrogen partial pressure decreases the char yield and conversely increases the yield of gas and liquid (compare Runs 5 and 7).

The concentration of molybdenum recovered with the fines in the supercritical distillation residue of Run 5 is quite high at 13.5 wt. %, indicating a technique for catalyst recycle. A molybdenum balance shows that 20% of that charged remained in the coal char in the basket. The concentration level of 1.5 wt. % is on the same order as that used in the tests reported by Weller (10). It is likely that the catalyst will be effective at much lower concentrations. Back extraction into acidified water is one means of recovering the catalyst for recycle.

The coal tar produced in Run 5 has a sulfur content of 1.7 wt. %, reduced from the 3.7 wt. % in the feed coal. The char has only a slightly lower sulfur content (3.6 wt. %) than the feed. The coal liquid produced in Run 7 has a viscosity of

5.3×10^{-4} m^2/s at 310.9°K (530 cSt at 100°F), which places it in the same viscosity range as SAE 70 lube oil. The C/H ratio of the tar in Run 5 is 1.1.

COMPARISON TO LITERATURE DATA

In the present work, on a moisture and ash free basis the yield of gas and liquid is 54 wt. % and the yield of char is 46 wt. % for the gasification/liquifaction of Illinois No. 6 coal with MoS_3 in supercritical water at 670°K, 4.6 MPa hydrogen cold charge pressure, and 30.4 MPa total pressure (Run 7). This can be compared to the 48 wt. % maf volatile content of the coal.

Batch liquifaction experiments performed at Oak Ridge National Laboratory (16) on extraction of Illinois No. 6 coal into supercritical toluene with KOH or NaOH catalyst and without hydrogen in 2 hours at 614-616°K and 23.9-27.3 MPa yielded 43 wt. % gas and liquid, maf basis. This is the same as that attained in Run 5 in the present work.

In coal liquifactions of Illinois No. 6 coal by Ross et al. (13) using water, Na_2MoO_4, 4.9 MPa CO charge pressure, and 673°K, the total yields of benzene soluble material and benzene insoluble material were 51 and 35% maf, respectively. With H_2 gas instead of CO, the corresponding yields were 38 and 47%. The yield of benzene insoluble material in the present study is 45 wt. % maf with a cold hydrogen pressure of 2.6-3.5 MPa (Run 5) and 39 wt. % maf with a cold hydrogen pressure of 3.5-4.6 MPa (Run 7). These data are comparable.

In conclusion, coal liquifaction with water-soluble impregnated catalyst, hydrogen/carbon monoxide reducing gas, and supercritical distillation to separate liquid product from solid product can provide an attractive product slate and deserves to be studied further.

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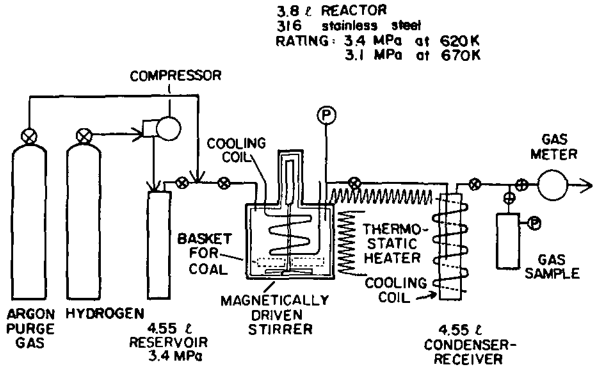

FIG. 1. APPARATUS FOR COAL HYDROGENATION AND DISTILLATION

Table 1

Operating Conditions for Hydrogenation of Illinois No. 6 Coal with Catalyst Dissolved in Water in a 3.8ℓ Stainless Steel Reactor

Run	1	2	3	4	5	6	7
Catalyst	←	$SnCl_2$		→	←	MoS_3	→
Coal Size	3.2 mm	←	Powdered	→	←	3.2 mm	→
Charge, g							
Coal (not dried)	146.9	77.8	89.0	488	235.5	225.6	212.3
Water	997	997	944	1000	1000	900	480
Catalyst	10.0	2.0	8.5	28.5	10.0	9.0	10.0
Hydrogen	6.2	9.4	12.8	>5.6	5.2-7.1[a]		9.5-12.2[a]
Temperature, °K	645-658	640-655	640-647	644-663	643-667	643-660	664-673
Pressure, MPa	23.3-31.2	22.3-28.8	24.0-34.2	25.0-34.3	28.0-34.6	27.7-33.6	29.0-31.3
Hydrogen pressure, MPa							
Initial (cold)	2.7	4.1	5.4	2.8	2.6-3.5[a]	4.2	3.5-4.6[a]
Final (hot, partial P)					5.5		6.4
Water density, g/cc	0.267	0.263	0.250	<0.288	0.273	0.245	0.130
Heatup time, hr	1.4	1.3	1.4	1.2	1.4	1.2	1.6
Equil. time, hr	2.0	1.6	2.1	3.9	2.0	2.3	3.5
Distillation	Slow Hot	Partial Hot	None	Slow Hot	Slow Hot	Instant Hot Flash	Slow Hot

[a] Additional hydrogen added during run

Table 2. Gas Yields and Analyses for Hydrogenation of Illinois No. 6 Coal With Supercritical Water and Soluble Catalyst

Run	2	4	5	7
Total Gas				
Yield, gmol	>2.4	>4.45	3.57	4.75
g	>14.8	>45.2	44.1	44.5
Mol % H_2	77.4	76.0	73.5	78.1
Mol % A, N_2, H_2O	10.0	11.9	22.1	11.5
Mole % Carbonaceous Gas	3.9	15.1	8.5	10.3
Mole % H_2S, NH_3	----	----	0.6	1.1
Gas Produced				
(H_2, A, N_2, H_2O free)				
Yield, gmol	>0.11	>0.72	0.380	0.589
g	>4.0	>21.9	13.7	19.6
Analysis, mol %				
CO	1.6	0.0	0.0	0.0
CO	53.6	40.7	42.1	35.4
H_2S, Mercaptan	----	----	>0.4	4.0
NH_3	----	----	6.2	5.9
Hydrocarbon				
C_1	23.9	30.2	18.2	26.5
C_2	11.0	16.1	14.2	14.2
C_3	6.7	8.8	13.2	11.6
C_4 & C_5	3.2	4.2	5.6	2.4

Table 3. Liquid and Solid Yields and Analyses for Hydrogenation of Illinois No. 6 Coal With Supercritical Water and Soluble Catalyst

Run	1	2	3	4	5	6	7
Aqueous Product							
Yield, g	---	---	939	976	1002	---	500
Solubles content, g	---	---	---	6[d]	5	---	0.4
Organic Liquid[a,b]							
Yield, g	---	16[c]	25[c]	55[e]	42	---	53
Pentane Solubles, wt. %	---	3	---	74[f]	71[f]	---	87
Benzene solubles, wt. %	70[f]	29	43	23	27	---	12
Pyridine solubles, wt. %	---	---	---	3	1	---	0
Solid Product[b]							
Yield, g	95	53	72	344	155	145	118
Pentane solubles, wt. %	---	---	---	6	1		2
Benzene solubles, wt. %	5	21	20[g]	2	2		8
Pyridine solubles, wt. %	---	---	---	6	12		23

[a] The yield includes tar decanted from aqueous distillate and residue recovered from acetone wash of walls.

[b] The benzene solubles in Runs 1, 2, and 3 include pentane solubles, determined using Soxhlet extraction with Gooch crucibles and asbestos mats. The solubles in Runs 4-7 were determined using Soxhlet extraction with paper thimbles, and the percentages listed are the incremental solubilities in each solvent.

[c] Includes aqueous solubles and probably catalyst.

[d] Volatile aqueous solubles residue.

[e] Includes aqueous solubles residue.

[f] Analysis of decanted tar only.

[g] Acetone solubles.

Table 4. Material Balance in Liquifaction Experiments

Basis: g/100 g coal (not dried)

Run	1	2	3	4	5	6	7
H_2 in	4.2	12	14	1.2-1.6	3.0	---	5.8
H_2 out	---	>5	---	>1.6	2.7	---	3.9
H_2 net	---	>-7	---	>+0.0	-0.3	---	-1.9
CO_2 (+CO) produced	---	>3	---	>2.7	3.0	---	4.3
H_2O in	---	1281	1061	205	425	399	226
Aqueous out[a]	---	---	>1055	>199	424	---	235
Gas Product	---	5	---	>4	6	---	9
Organic liquid product[b]	---	18[c]	19[c]	11	20	---	25
Solid product (minus catalyst)	58	68	81	65	61	60	51
(in - out)	---	---	---	>74	87	---	92

[a] Includes water content of gas. Organic distillate and residue recovered from distillation of aqueous product are included under organic liquid product.

[a] Includes residue recovered from acetone wash of walls.

[b] Minus catalyst.

Table 5. Ultimate Analyses for Liquifaction Experiments

Sample	Feed Coal	Run 5 Tar	Run 5 Char	Run 5 Fines
Moisture, wt. %	5.5		0.99	
Ash, includes Mo, wt. %	13.7		18.8	35.8
Dry Basis, wt. %				
Carbon	66.2[a]	81.6[b]	65.6	
Hydrogen	4.54	7.67	3.53	
Nitrogen	1.18	1.09	1.20	
Sulfur	3.74	1.71	3.64	
Molybdenum	---		1.5	13.5[b]

[a] Analysis of powdered coal

[b] Analysis not dry basis